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Research Article

Synthesis and Characterization of Limonene-Based Sulfur Polymer

Ramazan Orhan[1*], Ercan Aydoğmuş[2]

[1*] Fırat University, Faculty of Engineering, Department of Chemical Engineering, Elazığ, Turkey, (ORCID: 0000-0003-2287-4238), rorhan@firat.edu.tr
[2] Fırat University, Faculty of Engineering, Department of Chemical Engineering, Elazığ, Turkey, (ORCID: 0000-0002-1643-2487), ercanaydogmus@firat.edu.tr

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Abstract

In this research, a sulfur-based polymer has been synthesized with limonene extracted from orange peels. The synthesis process has been carried out by dropping limonene at 0 wt.%, 0.5 wt.%, 1 wt.%, 2 wt.%, and 4 wt.% ratios into the molten sulfur. The change in the chemical bond structure of the synthesized sulfur-based polymer is determined by Fourier Transform Infrared Spectrophotometer (FTIR). Moreover, the density, Shore D hardness, and thermal conductivity coefficient of the sulfur-based polymer are also characterized. According to the evaluations, it has been seen that limonene extracted from 1% orange peel gave the best results. It has been observed that the polymerization efficiency is low when used below 1 wt.% by mass. At higher rates, Shore D hardness of the sulfur-based polymer decreases, thus a softer polymer is obtained. Besides, the density of the sulfur-based polymer is approximately 2067 kg/m^3, and the thermal conductivity coefficient is measured at an average of 0.25 W/m·K. As the content of limonene in the polymer mixture raises, the thermal conductivity coefficient decreases and a more porous structure is formed.

Keywords: Limonene, sulfur polymer, synthesis, characterization.

Limonen Bazlı Kükürt Polimerinin Sentezi ve Karakterizasyonu

Öz

Bu araştırmada, portakal kabuklarından ekstrakte edilen limonen ile kükürt bazlı bir polimer sentezlenmiştir. Sentez işlemi, erimiş kükürt içerisine kütlece % 0, % 0.5, % 1, % 2 ve % 4 oranında limonen damlatılarak gerçekleştirilmiştir. Sentezlenen kükürt bazlı polimerin kimyasal bağ yapısındaki değişiklik Fourier Dönüşümü Kızılötesi Spektrofotometresi (FTIR) ile belirlenmiştir. Ayrıca, kükürt bazlı polimerin yoğunluğu, Shore D sertliği ve termal iletkenlik katsayısı da karakterize edilmiştir. Yapılan değerlendirmelere göre en iyi sonuçlar ağırlıkça % 1 portakal kabuğundan ekstrakte edilen limonen ile elde edilmiştir. Kütlece % 1'in altında limonen kullanıldığında polimerizasyon veriminin düşük olduğu gözlemlenmiştir. Daha yüksek oranlarda limonene kullanımı kükürt bazlı polimerin Shore D sertliği azaltmış ve böylece daha yumuşak bir polimer sentezlenmiştir. Ayrıca, kükürt bazlı polimerin ortalama yoğunluğu yaklaşık 2067 kg/m^3 ve ısıl iletkenlik katsayısı da 0.25 W/m·K olarak ölçülmüştür. Polimer karışımındaki limonen içeriği arttıkça ısıl iletkenlik katsayısı düşmüş ve daha gözenekli bir yapı oluşmuştur.

Anahtar Kelimeler: Limonen, kükürt polimeri, sentez, karakterizasyon.

1. Introduction

Sulfur, the most abundant element in the universe has been used for many centuries as an antibacterial agent, in gun powder formulation, fabric bleaching, and more recently vulcanization for latex [1-3]. Today, sulfur is a waste by-product of the petroleum refining industry (purification of crude oil and gas reserves), where SO2 is removed and converted, by hydrodesulfurization, to S8 [4]. Over 70 million tonnes of sulfur is produced annually, with only a small fraction of this being used for the production of commodity chemicals such as sulfuric acid and fertilizers [5, 6]. Despite this, as production outstrips demand, it poses a large of sulfur stocks and a global problem known as the "excess sulfur problem" in the petrochemical industry. Therefore, this unwanted elemental sulfur needs to be converted into useful materials for commercial applications. Sulfur polymers are a candidate to consume this excess sulfur and become an alternative to traditional synthetic polymers.

Sulfur exhibits unique thermal transitions from orthorhombic to monoclinic at around 95 °C (a solid-solid state transition) and begins to melt into a yellow liquid when heated to 120°C [7]. Above 160 °C, the molten sulfur undergoes ring-opening polymerization and becomes an amorphous, viscous material, and its color darkens from yellow to orange and finally to red. With increasing temperature, the viscous sulfur transforms into a red-colored high molecular weight poly-sulfur at about 200°C. It should be noted that even the color changes of sulfur are a mystery and a matter of debate, with Meyer stating in his study that when polymeric sulfur is quenched as a thin film at 200 °C, its appearance is not red but yellow [8]. Meyer also concluded in another study that the overall red appearance arises from the presence of organic impurities, or the smaller sulfur molecules S3 and S4 [9]. However, the polymeric sulfur is thermodynamically unstable at room temperature and slowly reverts to the more stable cyclooctasulfur (S8), which makes it difficult to directly use these polymers for material application. The reverting could be due to the presence of active sulfur radicals in the chain terminal. Thus, the termination of active radicals is very important to reach a stable polymer. Pyun et al. reported that the inverse vulcanization technique allows the stabilization of sulfur polymers by a small organic molecule such as 1,3-diisopropenyl benzene, which acts as a crosslinker against depolymerization [5].

The resulting polymers were given the name poly(sulfur-random-(1,3-diisopropenyl benzene)), and are written in shorthand here as poly(S-r-DIB), where "S" represents sulfur, "r" refers to the random nature of the binding, and DIB represents the aforementioned co-monomer. In general, this process affords statistical copolymers with randomized connectivity of sulfur and DIB co-monomer units, thus various concentrations of co-monomer may be included in the polymers. In the literature, various petro-based monomers such as divinylbenzene [10], dicyclopentadiene [11], ethylene glycol dimethyl acrylate [12] have been investigated to be copolymerized with sulfur employing the inverse vulcanization process. However, these monomers used are relatively expensive compared to sulfur. Therefore, there has been increased interest in using edible, economical, and low-cost bio-based crosslinkers such as limonene [13]. Sulfur polymers produced using the inverse vulcanization process have shown promising properties in various applications such as active material for Li-S battery [14], mercury capture [15], hydrocarbon removal [16], adhesives [17], infrared optics [18], and fertilizers [19].

In this research, firstly, limonene obtained under laboratory conditions is used as a crosslinker. The physical and chemical changes in the structure of the sulfur-based polymer produced by using limonene in different mass ratios have been evaluated. Optimization studies of the polymer obtained following the intended use are made and the main effective parameters are determined.

2. Material and Method

In this study, orange peels are extracted under experimental conditions and the oil phase is separated with a separatory funnel. Limonene solutions, which are present in large amounts in the oil phase, are prepared in different proportions by mass. In addition, homogeneous melting of powdered sulfur is ensured at 130 °C. The temperature of the mixture prepared under experimental conditions is increased up to 180 °C, and limonene is added dropwise and mixed. Mixing is done for about 10 minutes for both color change and gelation to occur in the mixture. The resulting sulfur-based polymer is poured into standard molds and waited 24 hours for curing. It has been made for the synthesized product for some physical and chemical characterization processes.

Figure 1 shows the synthesis process of limonene from orange peel under laboratory conditions. There is a high content of limonene (oil phase) in the extract phase. After various purification and chemical characterization processes, limonene is prepared for polymerization.

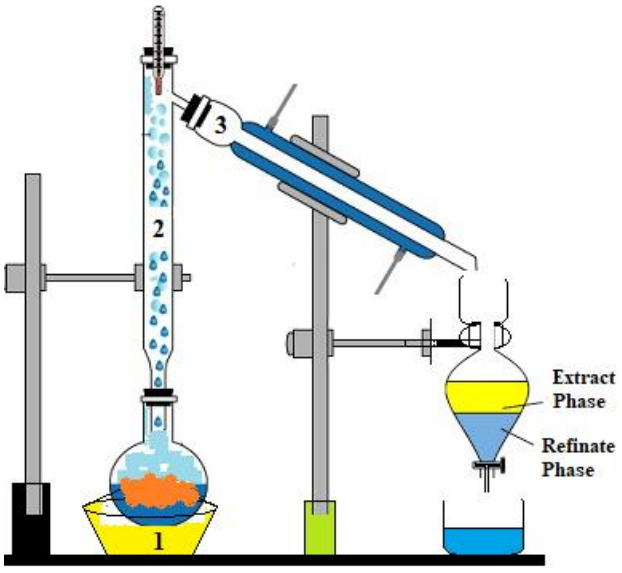

Fig. 1. Experimental scheme of the synthesis of limonene from orange peel (1: heating, 2: extraction column, 3: condenser system, and separatory funnel)

The chemical formula of limonene obtained from orange and lemon peels is shown in Figure 2.

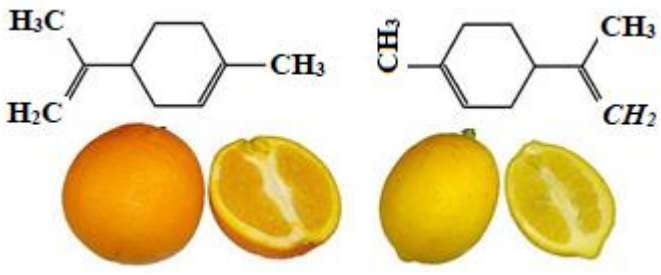

Fig. 2. The chemical formula of the synthesis of limonene

3. Results and Discussion

The properties of the synthesized polymer performed under laboratory conditions are given in Table 1.

Table 1. Experimental results for sulfur polymer

Limonene (wt.%)	Shore D Hardness	k (W/m·K)	ρ (kg/m^3)
0.0	34	0.27	2074
0.5	41	0.26	2070
1.0	57	0.25	2067
2.0	52	0.23	2058
4.0	48	0.21	2045

It is seen in Figure 3 that the synthesized polymer reached the maximum Shore D hardness at the optimum limonene ratio (1 wt.%).

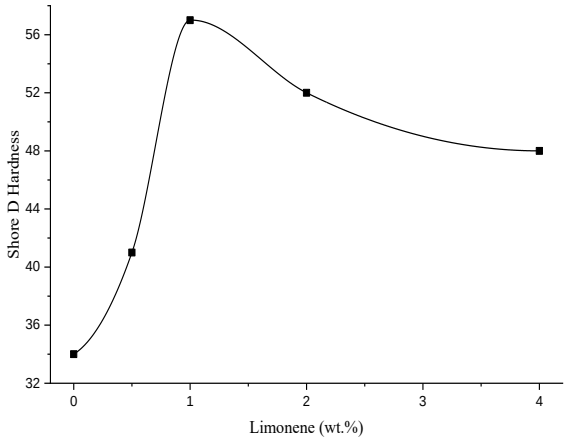

Fig. 3. Variation of Shore D hardness of sulfur-based polymer with limonene ratio

Increasing the content of limonene increased the porous structure of the sulfide-based polymer and decreased the thermal conductivity coefficient (Fig. 4.).

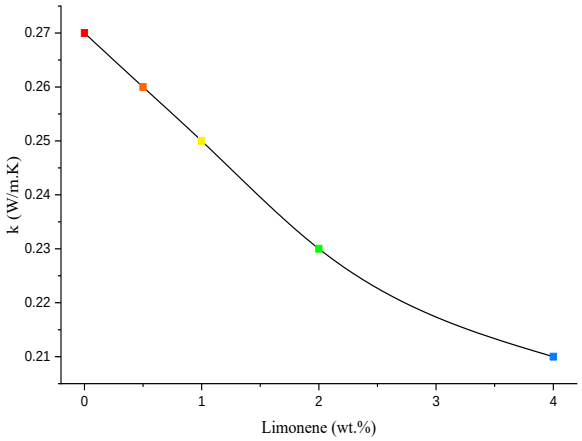

Fig. 4. Change of thermal conductivity of sulfur-based polymer with limonene ratio

In Figure 5, it has been determined that as the content of limonene increases, the density decreases in the sulfur polymer synthesized with bio additive.

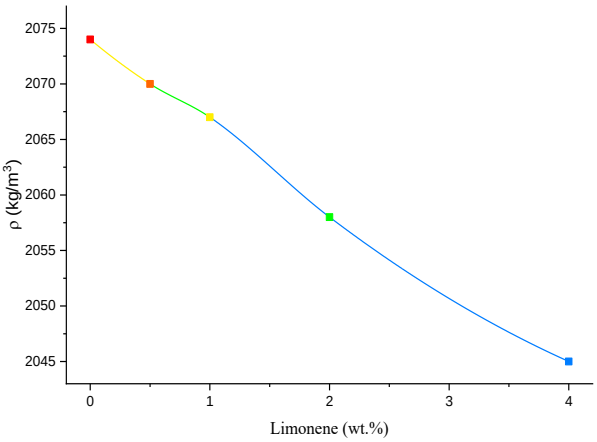

Fig. 5. Variation of the density of sulfur-based polymer with limonene ratio

According to the FTIR (Fig. 6), the peak in the spectrum of the sulfur powder showed that it is lost in the synthesized polymer, that is, it has been used in the cross-linking. Chemical bonds of limonene crosslinker have been determined in the sulfur-based polymer obtained in the FTIR spectrum.

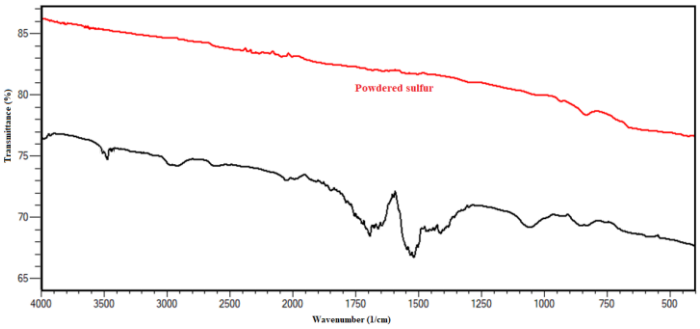

Fig. 6. FTIR spectrum sulfur and sulfur-based polymer

4. Conclusions and Recommendations

According to the results obtained, both the density and thermal conductivity coefficient of the sulfur-based polymer decreased as the ratio of limonene increased. However, Shore D hardness of the synthesized polymer reached its maximum at 1 wt.% limonene.

To synthesize limonene-based polymers, powdered sulfur must reach the boiling point. Limonene, which is synthesized from orange peels, should be dropped into the mixture to both increase the temperature and ensure a homogeneous mixture. Before the physical tests and chemical characterization of the obtained polymer, 24 hours should have waited for the curing.

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